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RADIATION CHEMISTRY LABORATORY SERIES

RESEARCH REPORT NO. 9

IRRADIATION "FACTOR-DEPENDENCY"

Some Vinyl Monomers: "Out-Scattering," "In-Scattering" and Non-Uniformity of Scanning Beam

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QUARTERMASTER RESEARCH & ENGINEERING CENTER

PIONEERING RESEARCH DIVISION

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A D D E N D U M

The term "in-scattering" as used in this report designates the composite effects of "forward-scattering" as the electrons penetrate the upper wall of the tube and "back-scattering" as they impinge on the inside of the tube. The blue cellophane film records, accordingly, the composite effects of the "forward-scattering," the impingement of the electrons on the film, and the "back-scattering."

Additional data at different energy levels of the electrons is presented by the tabulation on the reverse side of this sheet. The results are interpreted in the notes to the table. These data confirm the data presented in this report and are, consequently, in agreement with the general conclusions relative to the data presented.

The delivered dose for the results of Table 1, page 17, was 6 megarads, from a 2 Mev electron accelerator. The dose rate was 2 megarads per exposure and the shuttle speed was 46.5 inches per minute.

The readings of the 300 MSC blue cellophane films were taken promptly by use of a Beckman DU spectrophotometer, using a wavelength of 655 mμ, and a slit width of 0.87 mm. The precision of the measurements is of the order of a plus or minus 0.5% T, where T is the transmittancy of the film.

The data in the Delta % T column of Table I represent the net change in transmittancy of the 300 MSC blue cellophane film, which is obtained by subtracting the average control reading (19.9) from the respective average of the observed readings of the preceding column.

Change polyvinyl chloride, page 7, line 30, to 300 MSC blue cellophane film. Polyvinyl chloride filmn had been used previously, but the 300 MSC blue cellophane film was used for obtaining the data given in Table 1, page 17.

Dosimetry Studies with 300-MSC Light Blue Cellophane Films

Mev	Dose Rate, Megarads/ Pass	Dose in Megarads	Number of Samples	Average % increase in Transmittance of 300-MSC strips on the inside bottom of the tube over those on the outside top of the tube
3	1	4	40	36
2	1	3	24	50
1.5	1	4	10	8

Notes: The test tubes used in these studies were made from Corning glass 9800, were about 1 inch in diameter, and had an average wall thickness of about 50/1000 of an inch.

The film was placed on top of the tube (outside) and on the bottom of the same tube (inside) in order to obtain comparable readings for the absorbed dose on the outside and inside of the same tube as viewed by the 300-MSC Light Blue cellophane film.

The conveyer speed in each case was 93 inches per minute for the passage of the sample under the scanning beam. Presently the increase in transmittancy of the "inside" over the "outside" samples is attributed to (1) the attainment of near peak ionization under the conditions employed, and (2) some contribution from both forward "in-scattering" as the electrons emerge on the inside of the tube and to backward "in-scattering" as they impinge on the inner surface of the bottom and sides of the reaction tube.

From the above tabulation, it is observed that the most increase of the "inside" over the "outside" effect was obtained at an energy level of 2 Mev. One may assume, therefore, that with a 3 Mev source, many of the electrons completely penetrate both walls of the tube and do not contribute as much to secondary ionization. By use of a 1.5 Mev source, many of the electrons are spent before reaching the film in the bottom of the tube, and the overall effect results in only about an 8% increase for the "inside" film over that for the "outside" film.

FOREWORD

This report (Research Report No. 9 on Irradiation "Factor-Dependency" of the Radiation Chemistry Laboratory Series) presents: (1) substantial evidence for a balancing effect between "out-scattering" of radiation energy and "in-scattering," when one-inch pyrex tubes are used as the container for the irradiation-induced polymerization of vinyl monomers with an electron accelerator, and (2) data which indicate a non-uniformity of the order of about 9 per cent of the beam scan.

Data of Research Report No. 1, Styrene, indicate that factors such as atmosphere, degassing, diluent, dose, dose rate, moisture, and temperature all appear to be important parameters. Atmosphere, dose rate, and temperature were found to be statistically significant, with variations in dose rate being approximately twice as effective as variations in either atmosphere or temperature. With respect to molecular weight, temperature was found to be statistically significant at dose rates of 25,000, 50,000, and 100,000 rads per exposure. The non-additivity of dose was reported.

Research Report No. 2, Some Vinyl Monomers, gave results which indicate that under the experimental conditions employed: (1) polymerization rate is not equal to $kI^{1/2}$, (2) the E-value ("G_e"-value or amount of polymer obtained per unit of radiation energy) decreases with an increase in dose rate, (3) there is a non-additivity of dose, and (4) unless parameters are critically defined, the formulation of reaction rate has no significance.

Research Report No. 3, Styrene with Additives, provided data from which it was concluded for the additives used that: (1) the effect of an additive is a function of dose rate with respect to both molecular weight and conversion to polymer,

and may either catalyze or inhibit polymer formation, (2) the molecular weight decreases with an increase in dose rate for all additives used, (3) there appears to be an inverse ratio with respect to conversion and molecular weight, and (4) the efficiency of polymerization decreases markedly at the higher dose rates used in these studies.

In Research Report No. 4, Irradiation Cycle, it was concluded that: (1) a cycle of something more than three minutes at 75° C. is the most efficient for the irradiation-induced polymerization of certain vinyl monomers, (2) the better relative efficiency of a time cycle over continuous irradiation decreases with an increase in dose rate, (3) efficiency decreases markedly at the higher dose rates used in these studies, (4) reaction rate formulations, derived under experimental conditions different from those used in this study, are not applicable, and (5) the most desirable time cycle and temperature are functions of the monomer system.

Research Report No. 5, Degassing, presented experimental results from which it was concluded that: (1) degassing may significantly increase the conversion to polymer obtained by the irradiation-induced polymerization of vinyl monomers, and (2) the relative importance of degassing is interdependent on (a) the monomer system, (b) the dose rate, and (c) in certain cases at least, the presence of an inert atmosphere such as argon.

From data on the composite effect of degassing and the irradiation cycle, Research Report No. 6, it was concluded that: (1) with the other parameters used in this study, an irradiation cycle of more than three minutes is required for optimal conversion to polymer at a given dose rate and dose level, (2) both the effect of degassing and the irradiation cycle are dependent to some extent on the monomer system, (3) degassing is more dependent, with respect to its effect, on the monomer system than is the irradiation cycle, and (4) the relative composite effect of degassing and the irradiation cycle decreases in general with an increase in dose rate and total dose.

From the data obtained in a study of multiple parameters for the irradiation-induced polymerization of certain vinyl monomer systems (Research Report No. 7), it was concluded that the effect of: (1) air is dependent on the monomer system, (2) flame-out of the tubes under vacuum before introduction of the monomer is dependent on the chemical entity, (3) degassing once, twice, or three times is dependent on the monomer system, and (4) the combination of flame-out and degassing is also a function of the monomer system.

From the results presented by the eighteen graphs of Research Report No. 8 it was concluded that the effect of dose rate on the irradiation-induced polymerization of vinyl monomers is: (1) a function of the monomer systems, but with increase in efficiency with decrease in dose rate, (2) interdependent on the experimental conditions and operational parameters, and (3) is not in conformity with the $kI^{1/2}$ formulation, which was derived under different experimental conditions.

Table of Contents

Irradiation "Factor-Dependency": Some Vinyl Monomers; "Out-Scattering," "In-Scattering," and Non-Uniformity of the Scanning Beam

By

Ed. F. Degering, Gerald J. Caldarella, and Flora E. Evans

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A. Introduction

The so-called "back-scattering" or "out-scattering" of radiation energy when accelerated electrons impinge on a surface has been recognized for some time. Considerable effort has been devoted to the development of techniques to correct for this loss,[1] but this laboratory has not encountered any reference to "in-scattering" when a container such as a one-inch pyrex glass tube is used. In some of our previous reports, we have used adjusted results where the formulation for obtaining such values is: "adjusted value" = (per cent polymerization × 100)/(per cent ionization). The per cent ionization is found by multiplying the average wall thickness of the tube by the density of the glass (2.23) and then interpolating from a graph developed by Trump, *et al.*[1] In arriving at the average wall thickness, twenty micrometer readings were taken.

B. Preparation, Irradiation, and Processing of Samples

The preparation, irradiation, and processing of the samples from which the data for the graphs in this report

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[1] Trump, *et al.*, *J. Applied Phys.*, *21*, 346 (1950). Also see Radiation Chemistry Laboratory Series, Research Reports Nos. 3 and 4 (November and December, 1960).

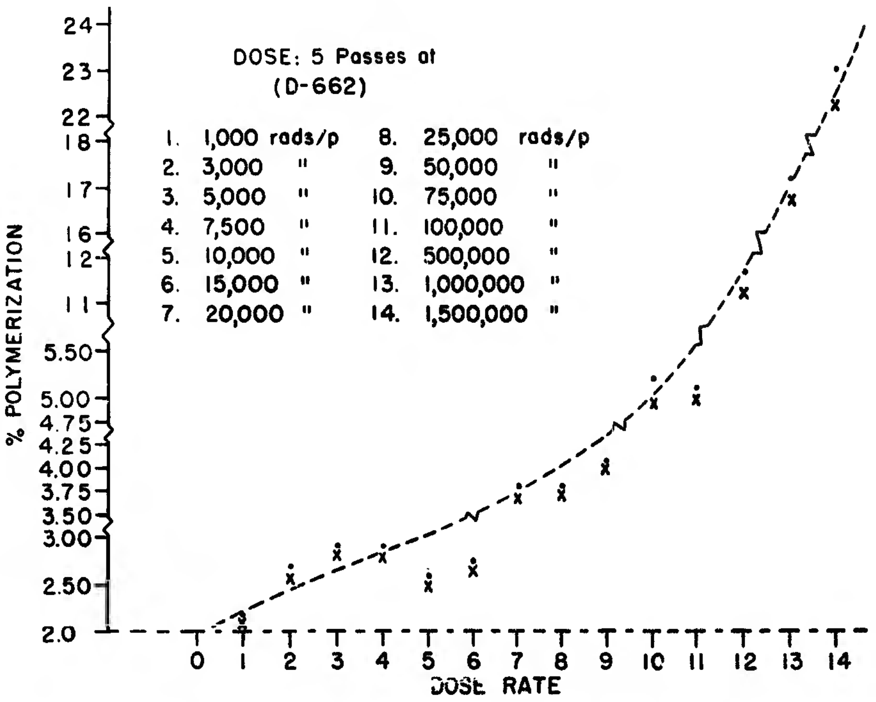

Figure 1. Styrene with no additive. Adjusted value, •; experimental value, x.

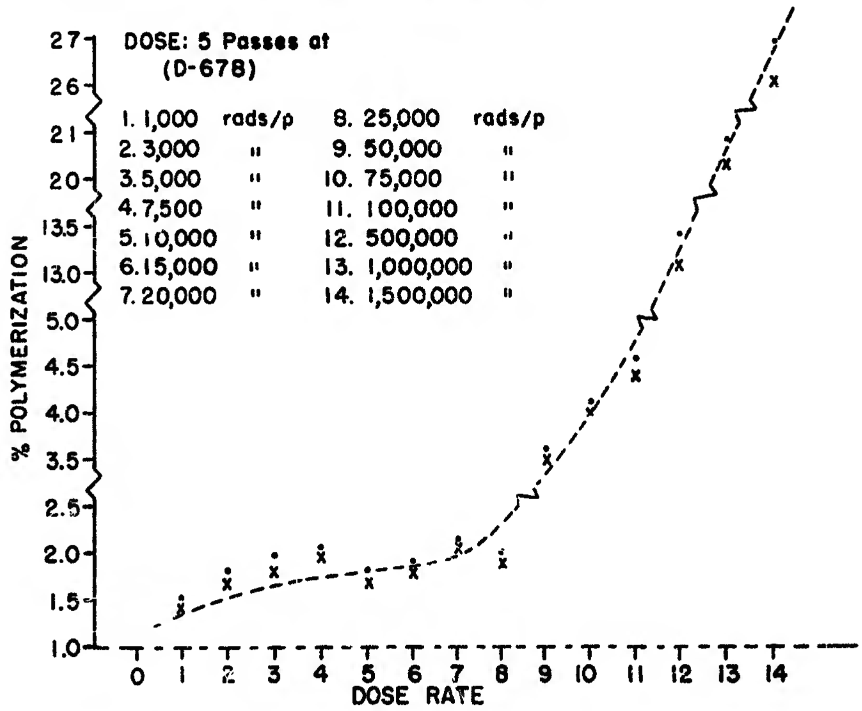

Figure 2. Styrene with no additive. Adjusted value, •; experimental value, x.

were derived, have been considered in detail in Research Reports Nos. 3, 4, and 8.[2] All samples were subjected to one degassing.

C. Experimental and Calculated Results

In Research Report No. 3 the effects of various additives at the one per cent level on the irradiation-induced polymerization of styrene were considered. These studies were made at fourteen dose rates and dose levels on a forty-five-minute cycle at 75° C.

One sample for a given additive was prepared for each of the first seven dose rates at the same time on the manifold and a comparable set was prepared for the last seven dose rates. Inasmuch as these samples were prepared in triplicate, the preparations of the samples for a given additive were made at six different times, with possible slight attendant variations in the preparative procedure.

When the samples were processed for per cent conversion to polymer, the one-inch pyrex tubes were cut and twenty micrometer readings taken on each tube. From the average wall thickness thus obtained, it was possible to calculate an adjusted value from the formulation given under Part A of this report.

These adjusted and experimentally determined values for per cent polymerization were then plotted as the ordinate against dose rate as the abscissa. On the abscissa, each point from left to right on the graphs represents both an increase in dose rate and an increase in total dose, as indicated

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[2] Degering, Ed. F., G. J. Calderella, Flora E. Evans, Stephen Grib, and Throop Smith, Radiation Chemistry Laboratory Series, Research Reports Nos. 3, 4 and 8 (November and December, 1960; June, 1961).

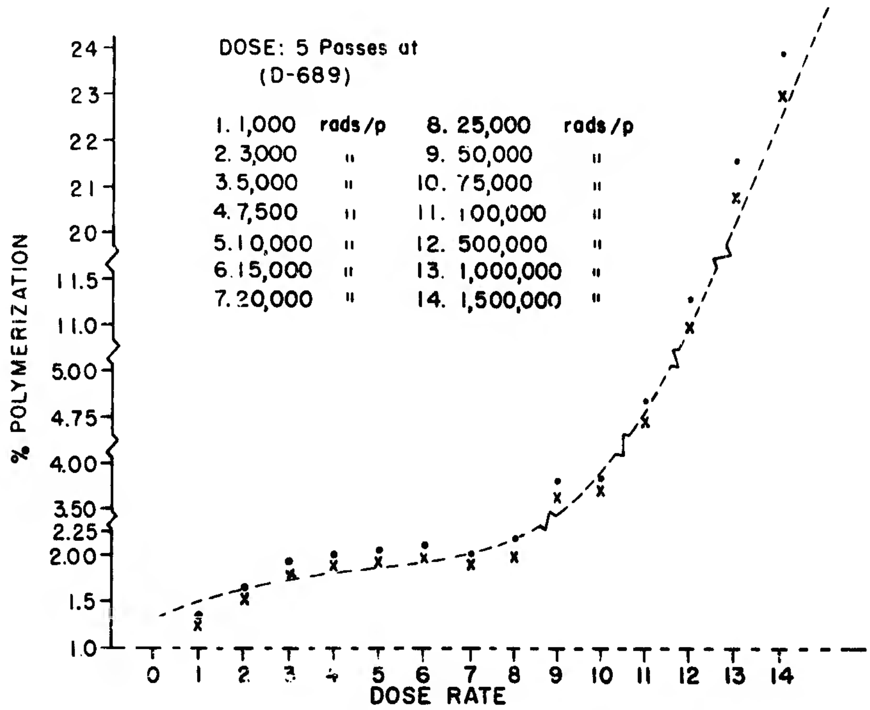

Figure 3. Styrene with no additive. Adjusted value, •; experimental value, x.

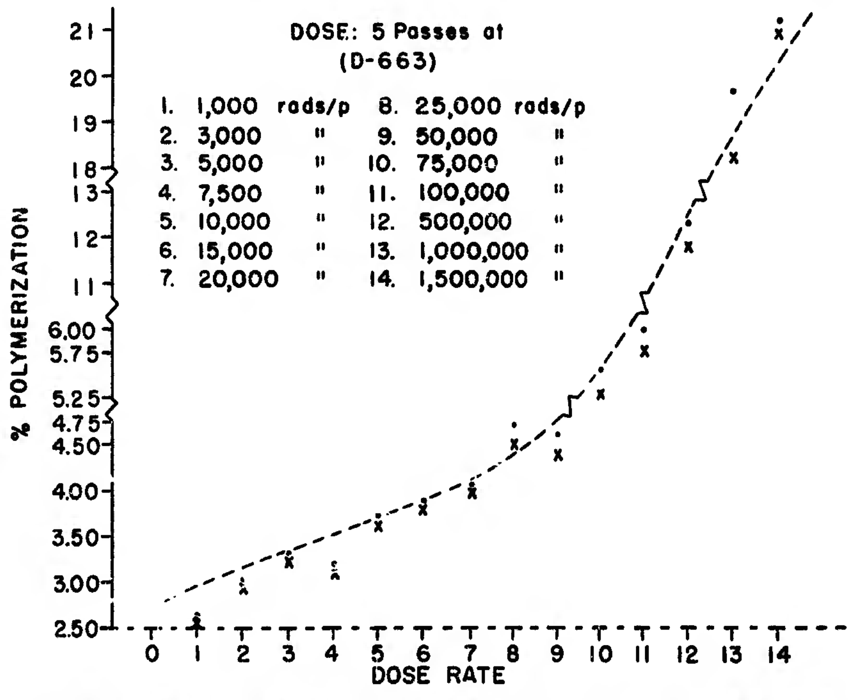

Figure 4. Styrene with 1% silicone oil 200. Adjusted value, •; experimental value, x.

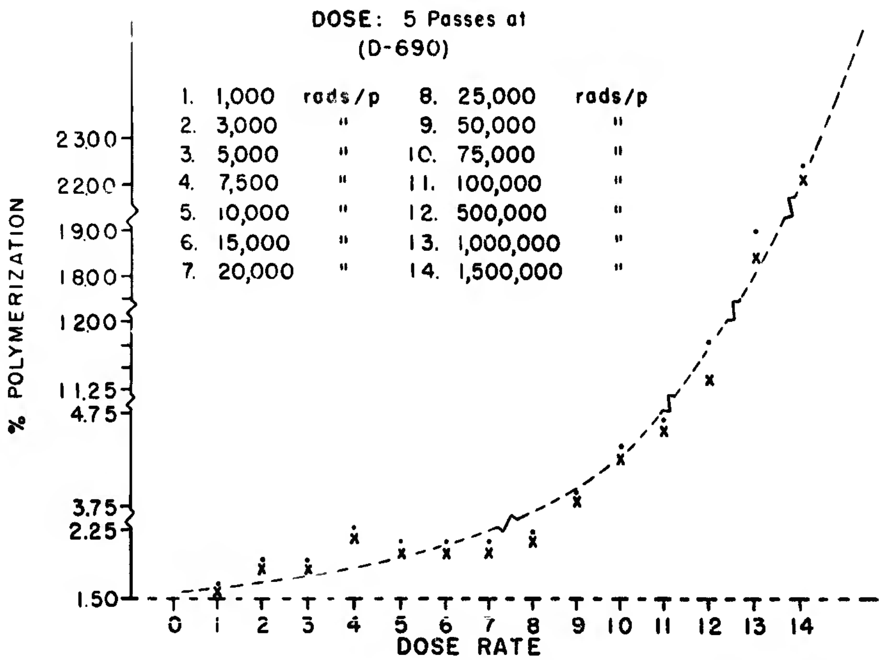

Figure 5. Styrene with 1% silicone oil 200. Adjusted value, °; experimental value, x.

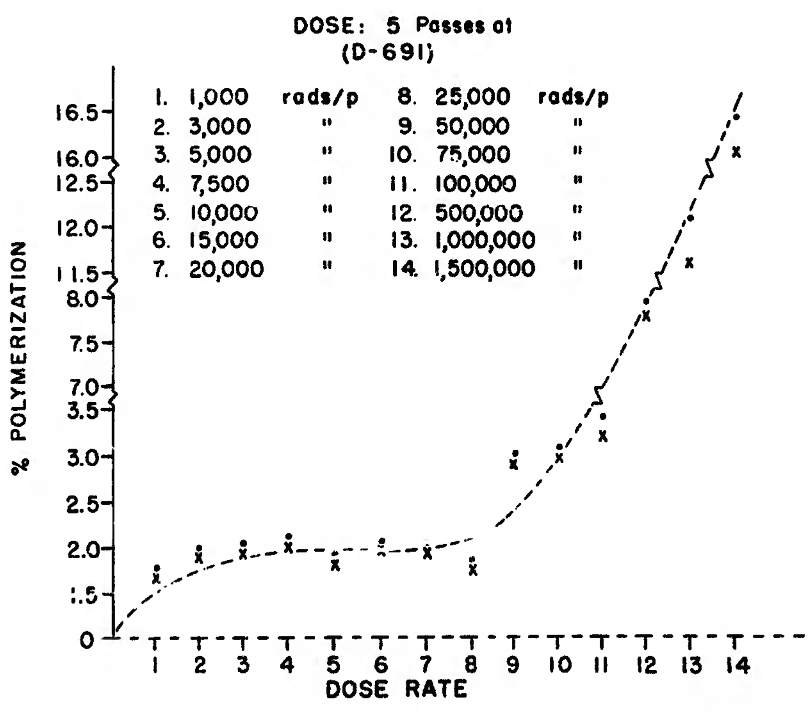

Figure 6. Styrene with 1% silicone oil 200. Adjusted value, •; experimental value, x.

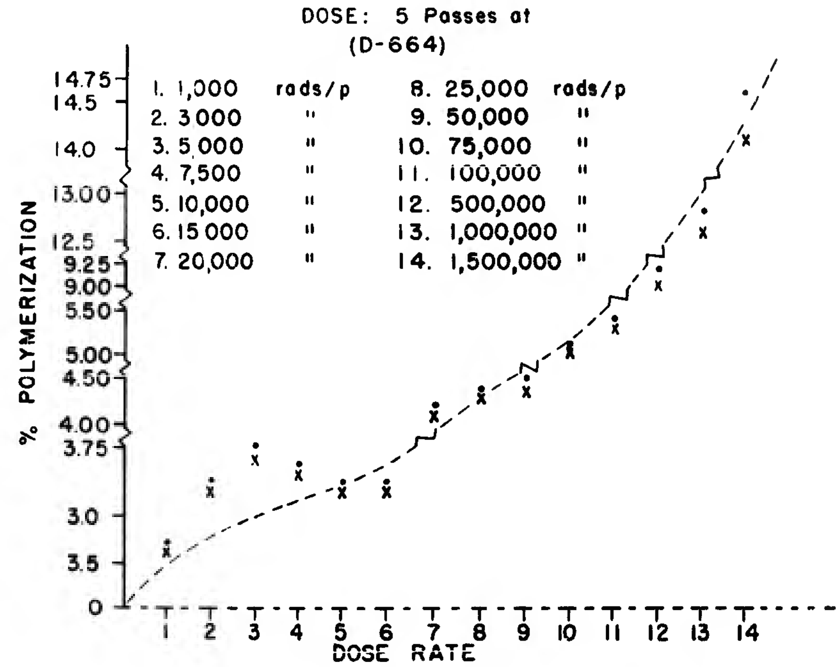

Figure 7. Styrene with 1% acrylic acid. Adjusted value, °; experimental value, x.

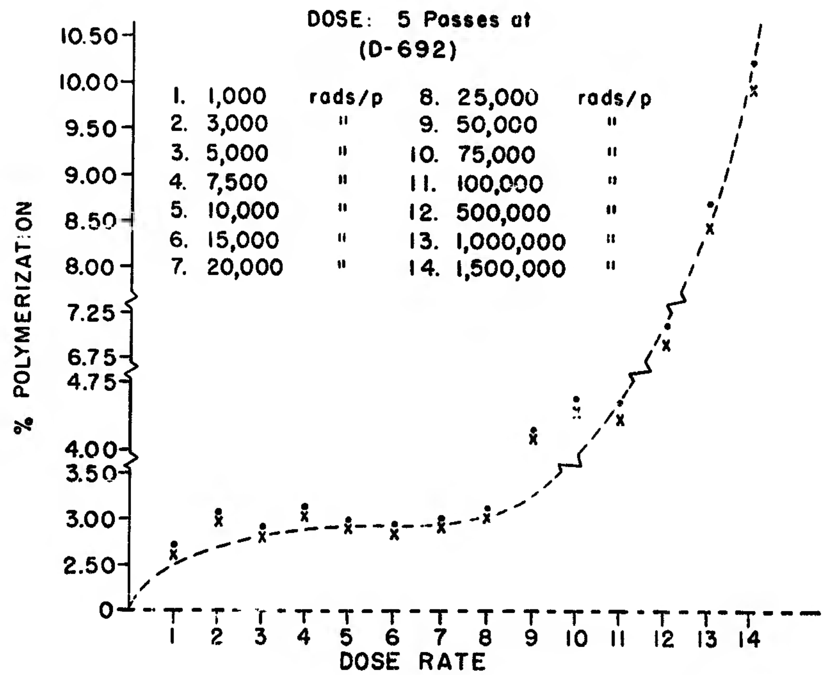

Figure 8. Styrene with 1% acrylic acid. Adjusted value, °; experimental value, °.

by the legend on the graph. In order to show the variations in the experimentally determined and adjusted values more adequately, broken or discontinuous ordinates and abscissa have been employed.

The results of this evaluation of data are shown as Figures 1 to 27, where graphs 1 to 3 are for the irradiation-induced polymerization of styrene with no additive, 4 to 6 are with silicone oil 200, 7 to 9 with acrylic acid, 10 to 12 with methacrylic acid, 13 to 15 with methyl acrylate, 16 to 18 with butyl acrylate, 19 to 21 with vinyl acetate, 22 to 24 with water, and 25 to 27 with acrylonitrile as the additive. In each case one per cent of the additive by volume was added to the styrene monomer.

It is obvious from an examination of these graphs that there is not an apparent significant difference, in general, between the plotted points for experimentally determined and adjusted values, particularly at the lower dose rates and dose levels. There is a tendency toward an increase in the spread between any two comparable points with an increase in dose rate and total dose. This is particularly true at the higher dose rates.

This consistency between the two sets of values may be explained tentatively by assuming that the shape of the irradiation tubes contributes significantly to "in-scattering," and that the "in-scattering" tends to retrieve approximately the same amount of energy to the monomer system under these experimental conditions as was lost by the effect of "out-scattering."

These results confirm dosimetry readings, made on the inside of the reaction tubes, on polyvinyl chloride, from which it was observed also that the radiation energy utilized on the inside of the tube was in each case approximately the same as that delivered to the outside of the tube. With a variation in wall thickness from 48.6 to 54.1 mil, the

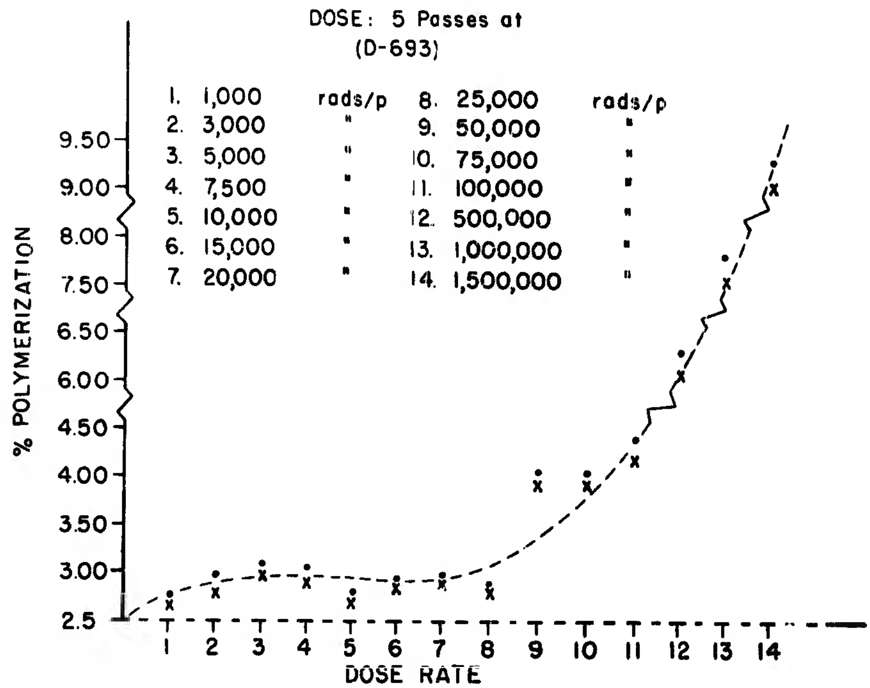

Figure 9. Styrene with 1% acrylic acid. Adjusted value, •; experimental value, x.

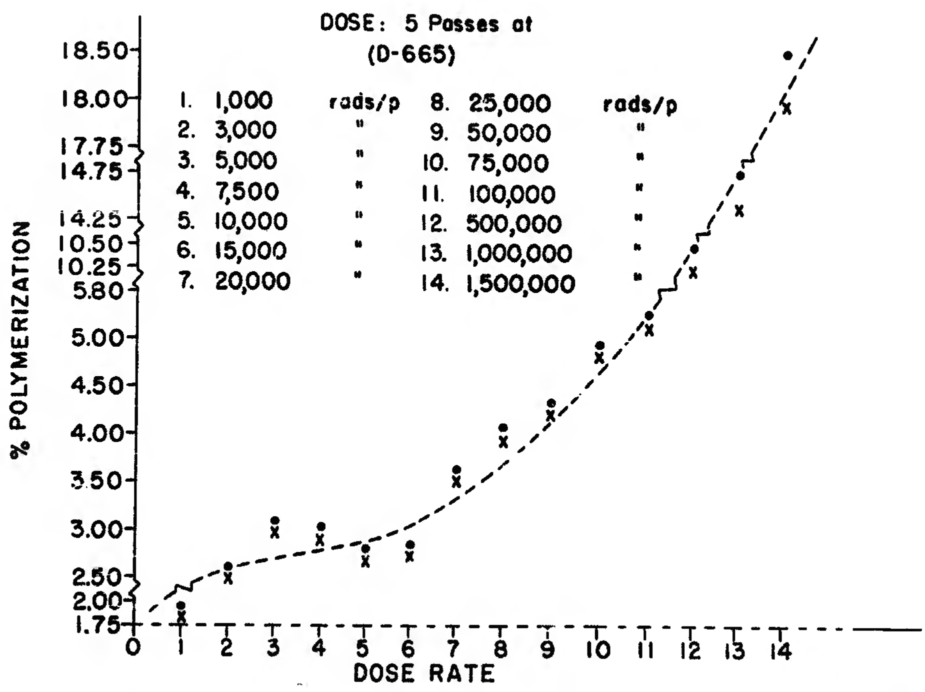

Figure 10. Styrene with 1% methacrylic acid. Adjusted value, •; experimental value, x.

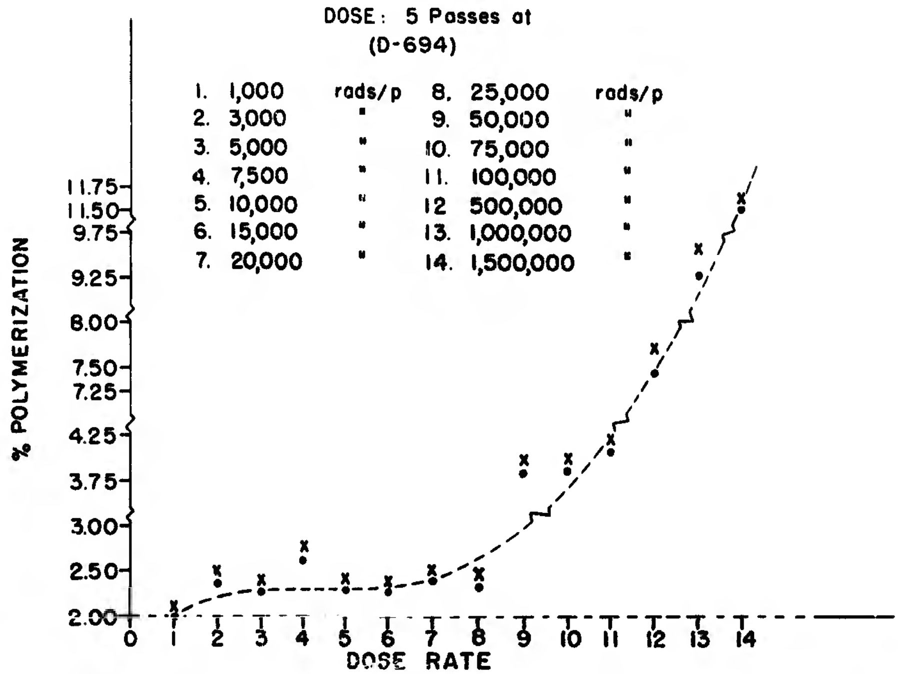

Figure 11. Styrene with 1% methacrylic acid. Adjusted value, x; experimental value, •.

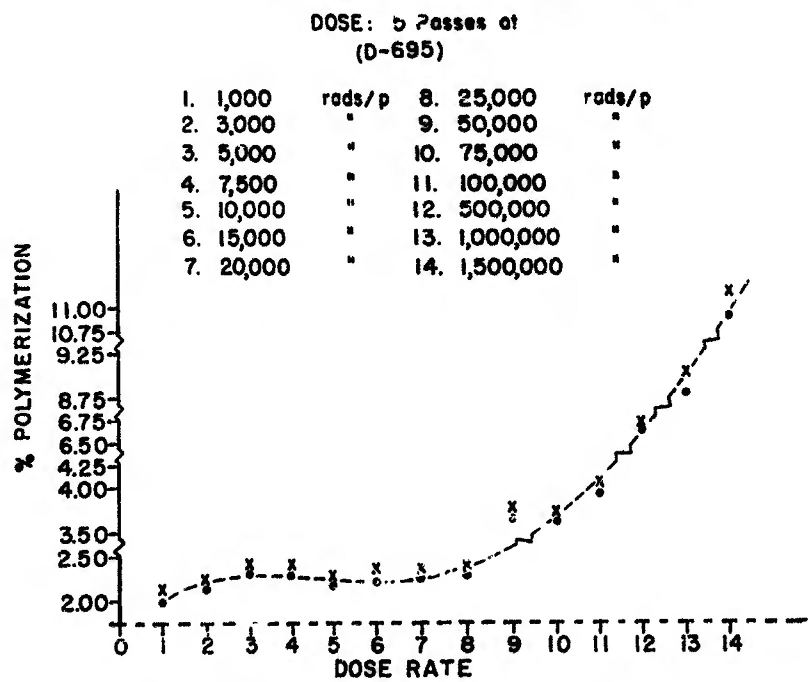

Figure 12. Styrene with 1% methacrylic acid. Adjusted value, x; experimental value, •.

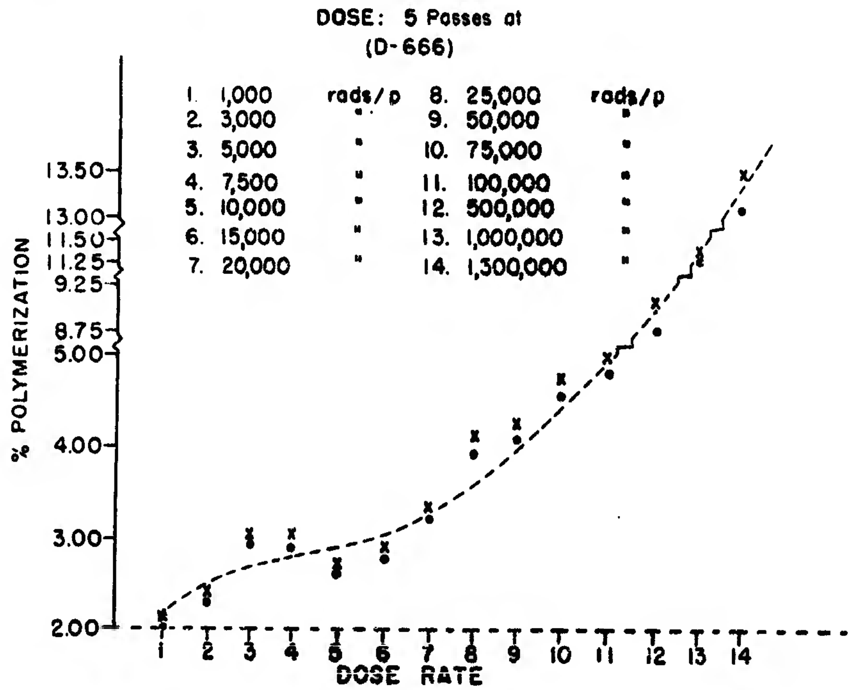

Figure 13. Styrene with 1% methyl acrylate. Adjusted value, x; experimental value, •.

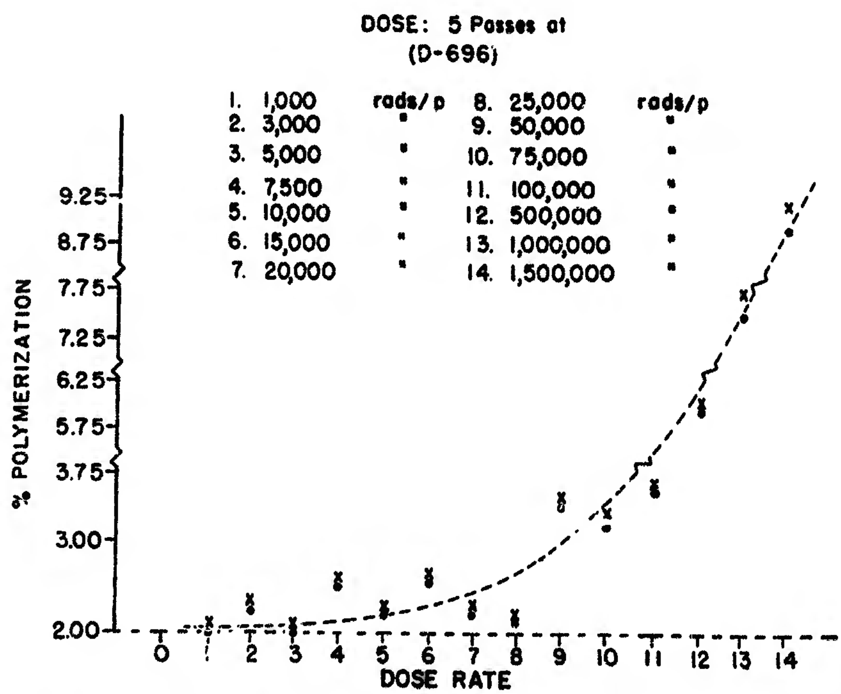

Figure 14. Styrene with 1% methyl acrylate. Adjusted value, x; experimental value, •.

corresponding per cent deviation in the plotted values for any point ranged from a minimum of 0.14 per cent to a maximum of 0.6 per cent.

The results obtained from measurements for dose delivered inside the tubes from a delivered outside-dose of 6 megarads are given in Table I. These ten tubes were arranged in order, left to right, under the beam in an attempt to determine the uniformity of the beam across the scan.

By inspection of the data of Table I it is observed that when the wall thickness of the tubes is relatively constant, the variation in the delivered dose is small as in the case of items 1, 2, and 3. The same holds for items 7 and 9, but when the data of item 1 are compared to those for items 7 and 9, the variations in both the wall thicknesses and the dose are much larger. This seems to suggest that wall thickness is an important parameter.

To what extent, however, the "in-scattering" contributes to the results is not completely apparent, particularly on the basis of these twenty-seven graphs where the results of "in-scattering" appear to be compensatory. If this be true and the results of Table I are approximately correct, the relative position of the sample under the scanning beam is also significant. The mean deviation across the beam for the delivered dose is of the order of 9 per cent, which suggests unfinished engineering with respect to the uniformity of the beam.

This report presents for the first time, accordingly, substantial data in support of a postulate for "in-scattering" of radiation energy under the experimental conditions used by the Radiation Chemistry Laboratory and for the balancing effects of "in-scattering" and "out-scattering." It presents data also relative to the non-uniformity of electron scanning beams.

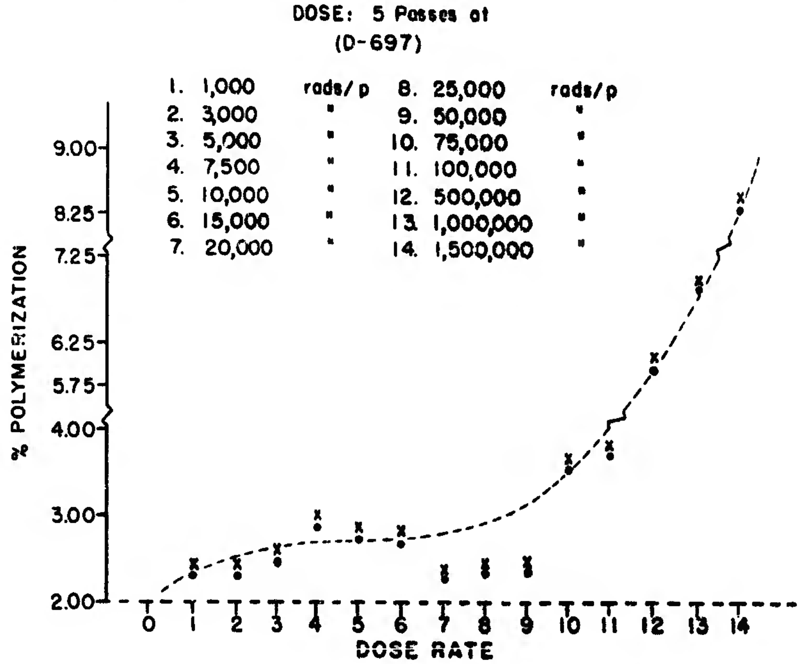

Figure 15. Styrene with 1% methyl acrylate. Adjusted value, x; experimental value, •.

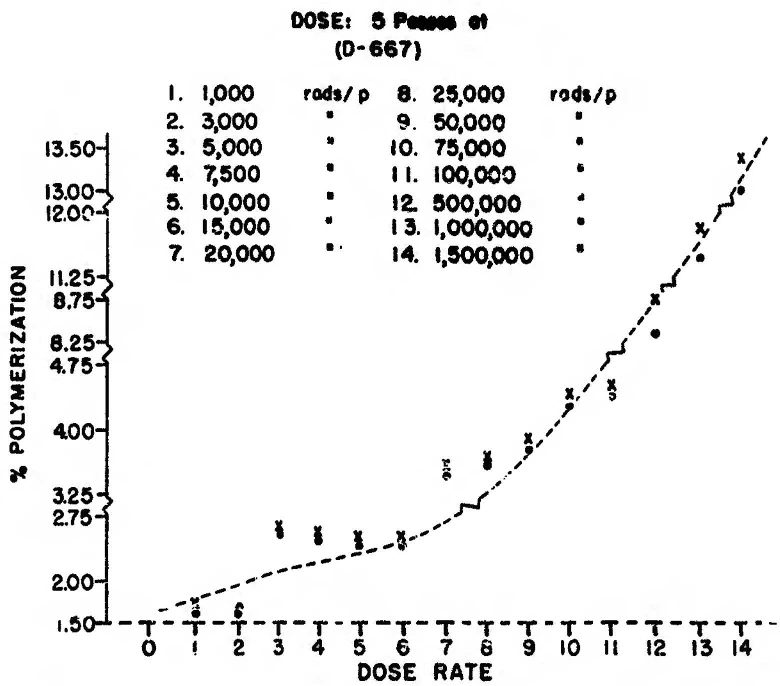

Figure 16. Styrene with 1% butyl acrylate. Adjusted value, x; experimental value, •.

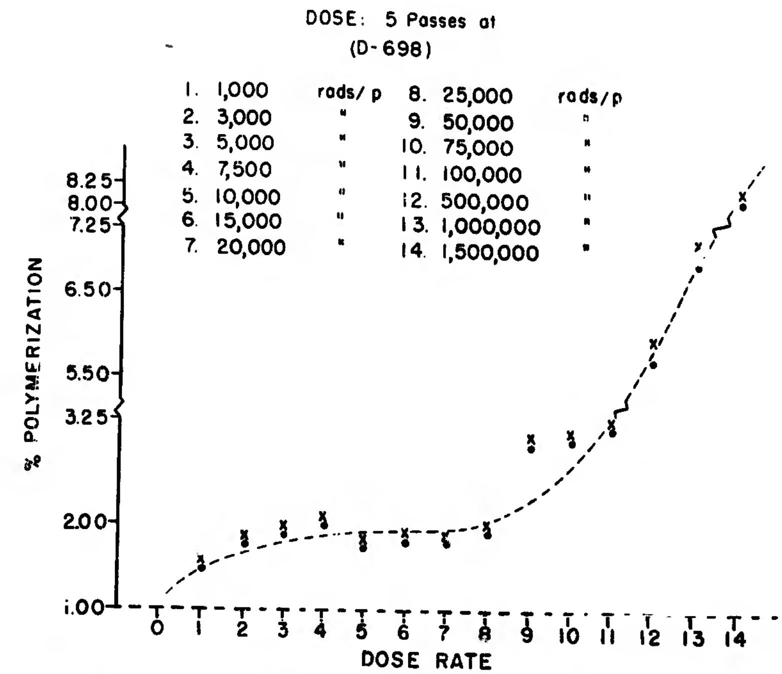

Figure 17. Styrene with 1% butyl acrylate. Adjusted value, x; experimental value, •.

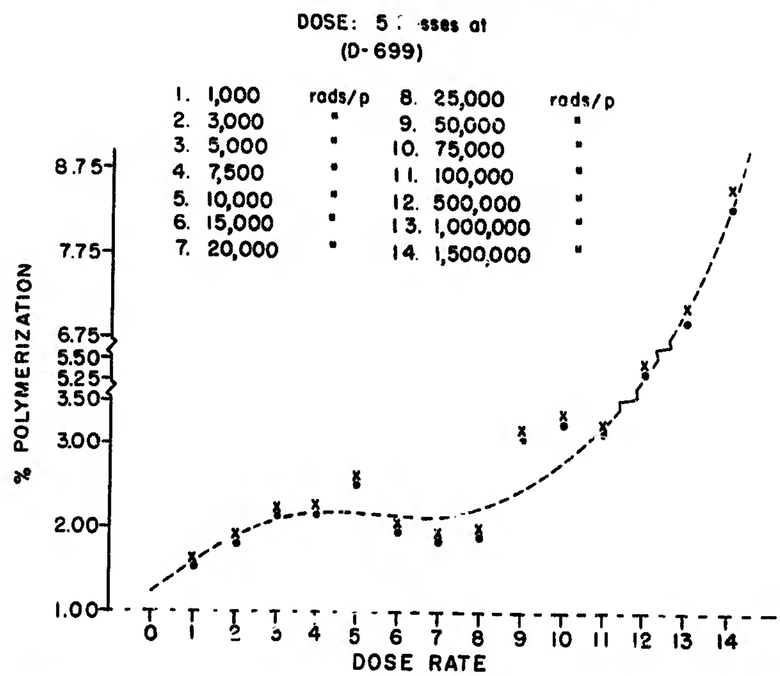

Figure 18. Styrene with 1% butyl acrylate. Adjusted value, x, experimental value, •.

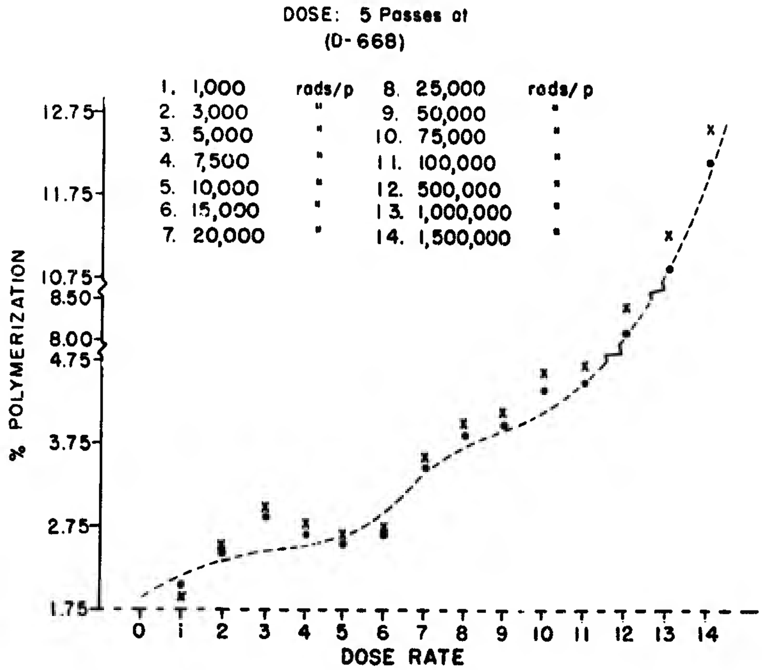

Figure 19. Styrene with 1% vinyl acetate. Adjusted value, x; experimental value, •.

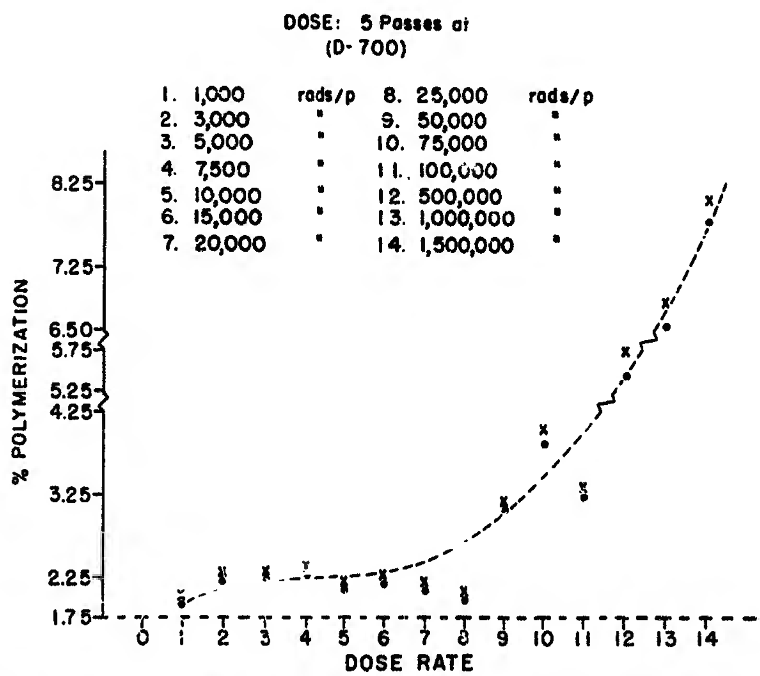

Figure 20. Styrene with 1% vinyl acetate. Adjusted value. x; experimental value, •.

D. Summary

From the experimental and adjusted values presented in the graphs, it is concluded that:

1. The "in-scattering" of radiation energy is significant under the experimental conditions and operational parameters used in these studies.

2. The "in-scattering" in each case, particularly at low dose rates and low dose levels, retrieves approximately the same amount of radiation energy as is lost through "out-scattering.

3. The non-uniformity of the beam scan used in this series of studies was of the order of 9 per cent.

E. Acknowledgements

The authors express their appreciation for the helpful assistance of: Mrs. Phyllis Zelezny for her painstaking care in the preparation of the manuscript copy, and W. H. Hall, who built the high vacuum system and prepared the sample tubes.

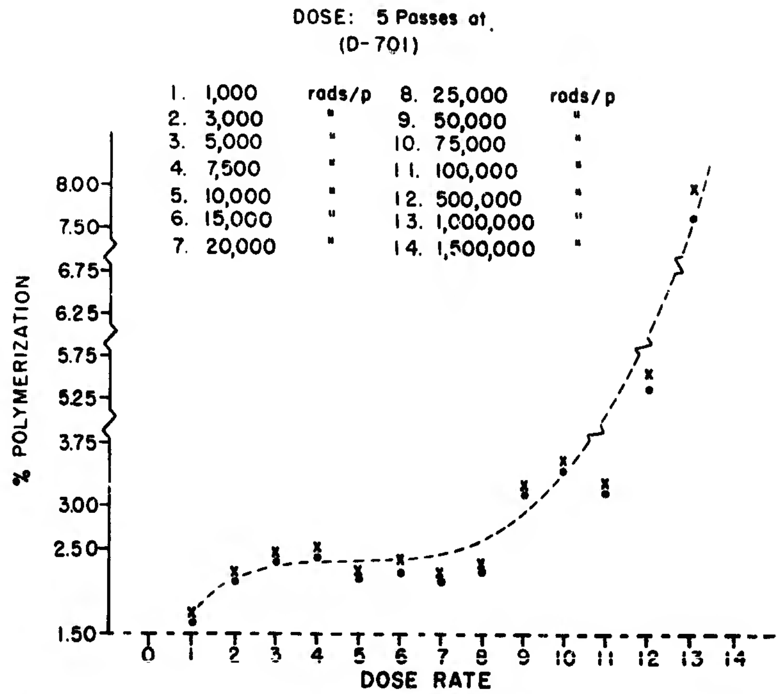

Figure 21. Styrene with 1% vinyl acetate. Adjusted value, x; experimental value, •.

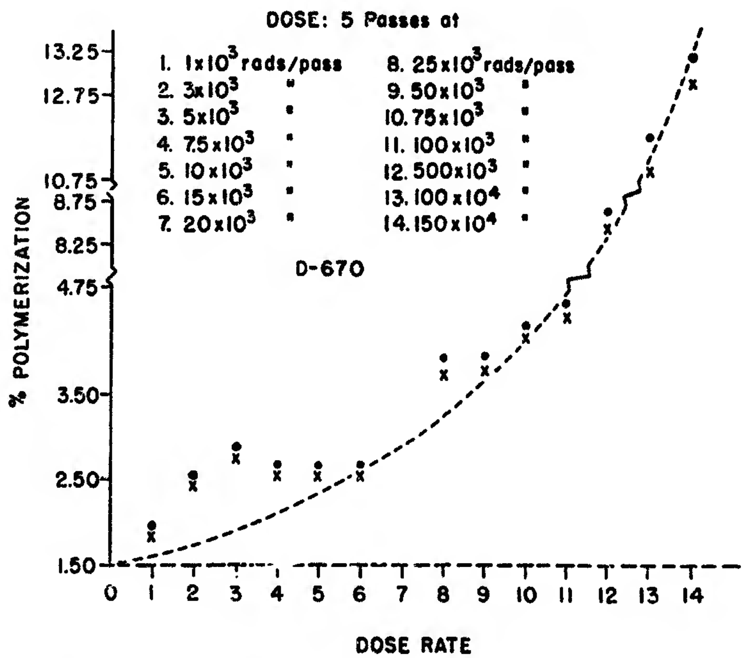

Figure 22. Styrene with 1% water. Adjusted value, °; experimental value, x.

TABLE I

Effect of Variations in Beam Scan and Wall Thickness of Radiation Tubes on Delivered Dose Inside of the Reaction Tubes (D-716)

Tube No.	Readings, % Transmittency Taken in Triplicate			Average % T	Delta % T	Dose Mr	Ionization from Curve	Wall Thickness
1.	37.6	38.6	38.6	38.2	18.4	5.2	99.02[1]	54.1 mil[2]
2.	38.4	38.2	36.9	37.8	17.9	5.0	98.11	51.2
3.	36.9	37.5	36.5	37.0	17.1	4.8	98.92	53.6
4.	36.6	38.7	37.3	37.6	17.7	5.0	98.92	53.6
5.	37.3	35.9	37.2	36.8	16.9	4.7	98.92	53.6
6.	41.0	39.3	38.8	39.7	19.8	5.6	97.51	49.4
7.	41.1	41.7	41.0	41.3	21.4	6.0	97.4	48.8
8.	40.0	41.2	40.8	40.7	20.8	5.9	98.7	52.9
9.	42.7	40.9	43.4	42.0	22.1	6.3	97.4	48.8
10.	40.7	40.5	40.7	40.6	20.7	5.8	97.33	48.6

[1] Taken from the graph developed by Trump, et al., J. Applied Phys., 21, 346 (1950).

[2] Each tabulated value is an average of twenty micrometer readings for the wall thickness of the respective tubes.

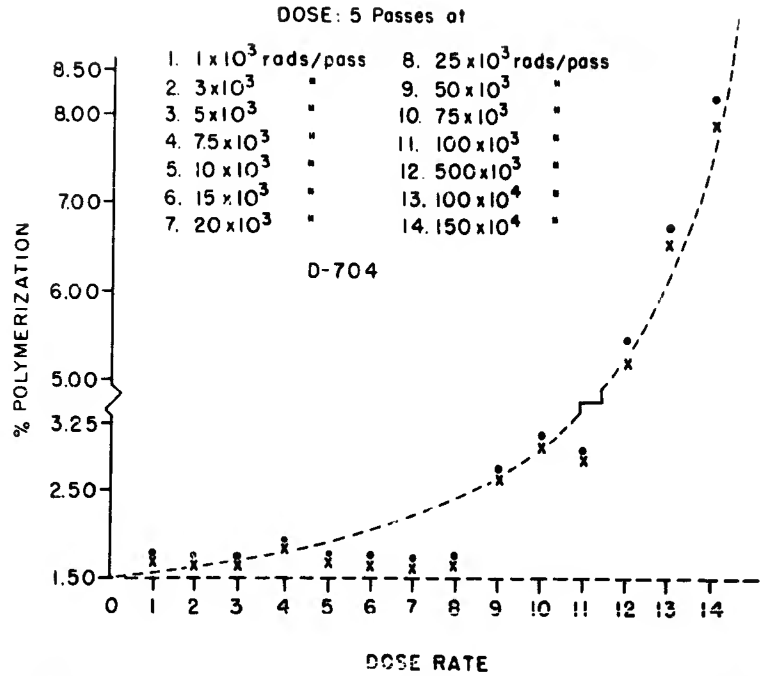

Figure 23. Styrene with 1% water. Adjusted value, •; experimental value, x.

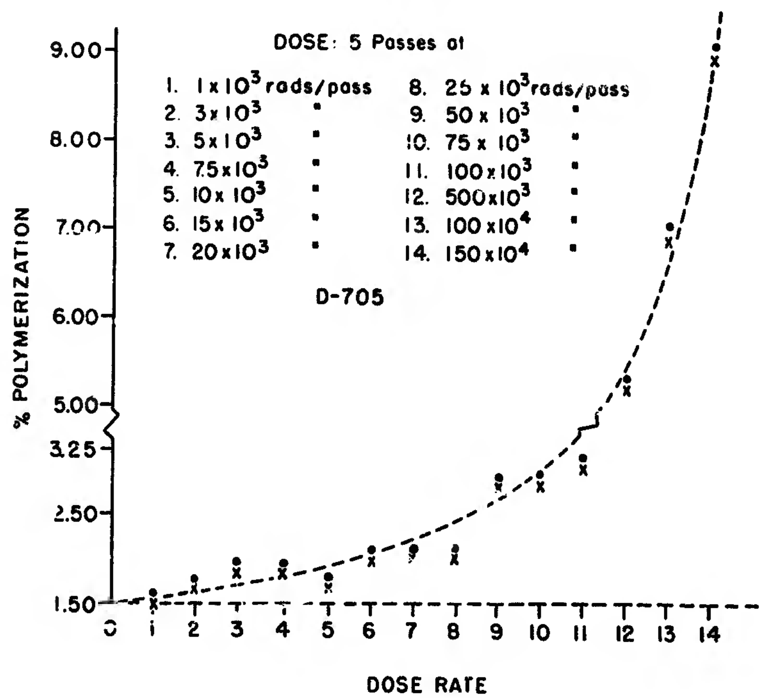

Figure 24. Styrene with 1% water. Adjusted value, °; experimental value, x.

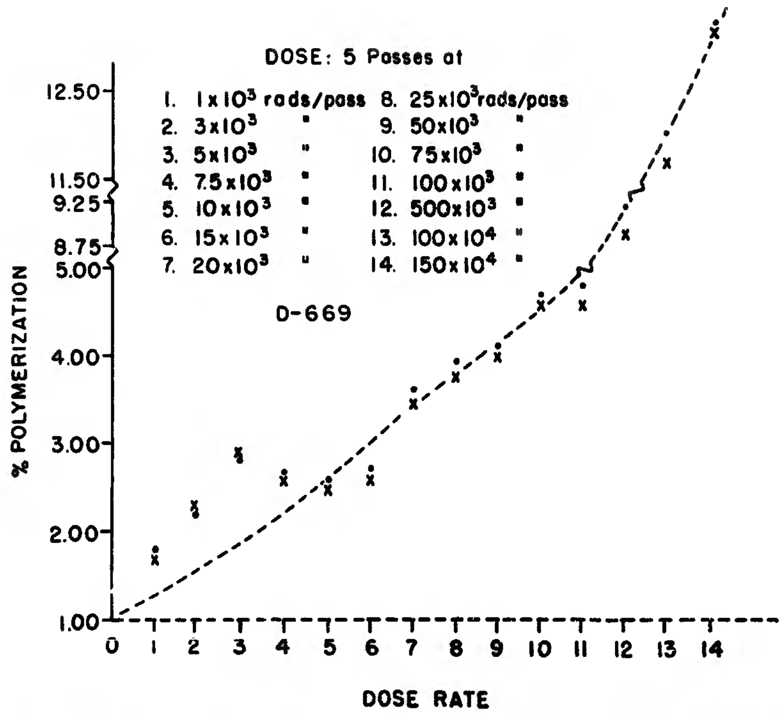

Figure 25. Styrene with 1% acrylonitrile. Adjusted value, •; experimental value, x.

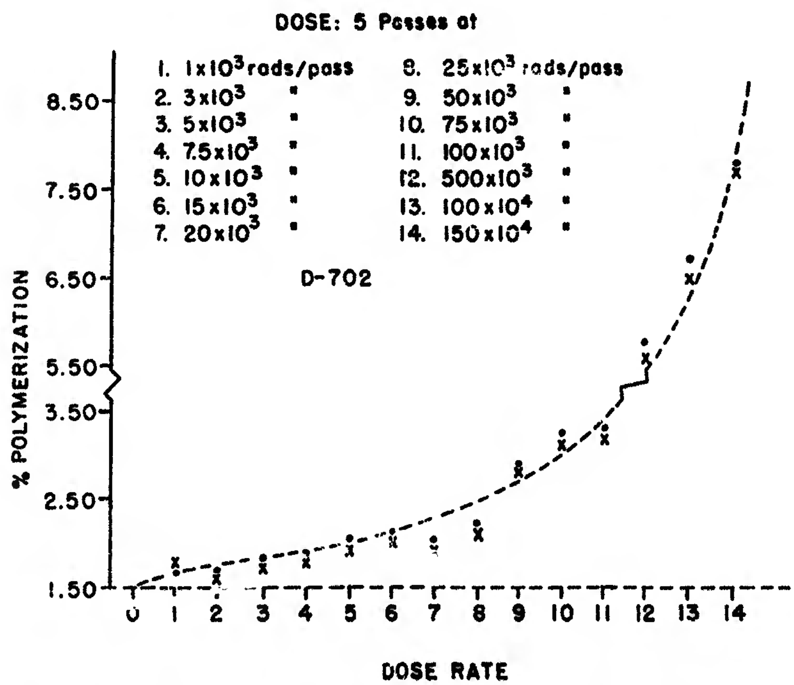

Figure 26. Styrene with 1% acrylonitrile. Adjusted value, •; experimental value, x.

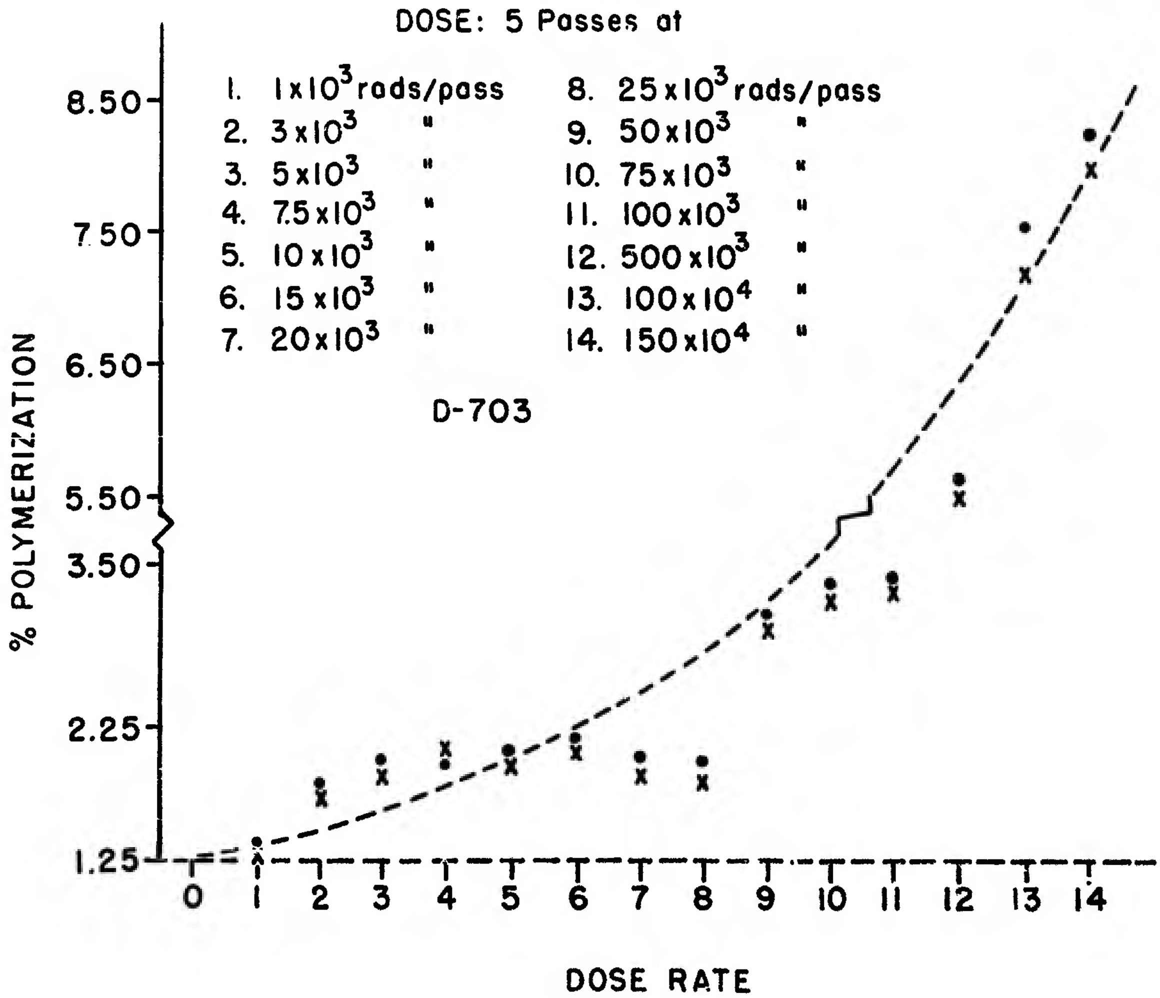

Figure 27. Styrene with 1% acrylonitrile. Adjusted value, •; experimental value, x.